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13. ABSTRACT *(Maximum 200 words)*
The objective of this work was to determine if C_{60} or its derivatives could enhance the oxidative thermal stability of JP-5 and similar aviation fuels. Two derivatives of C_{60} were prepared, n-hexyl amine and di-isopropylamine. Several conventional thermal stressing experiments were also performed: oxygen overpressure (OOP), isothermal corrosion oxidation test (ICOT), quartz crystal microbalance (QCM), and hot liquid process simulator (HLPS). In addition, a fuel stability test system (FSTS) developed at Advanced Fuel Research, Inc. (AFR) was also used. The FSTS includes fiber optic infrared transmission cells to assess fuel thermal stability during thermal stressing up to 500°C. The low temperature data from OOP, ICOT, QCM and HPLS show that pure C_{60} generally reduces the deposit formation, although the amount of this reduction is only modest (between 5 and 30%). The beneficial effects are larger under more severe conditions (higher temperatures, longer oxidation times, higher oxygen concentrations). The FSTS results were consistent with this trend, although at the highest temperatures (425-500°C), some potentially deleterious effects of C_{60} also appear to be enhanced. The effects of reactor tube activation were important for the FSTS. Additional work is warranted on exploring the beneficial effects of C_{60} addition which could serve to extent the operating range of common jet fuels.

14. SUBJECT TERMS
Thermal Stability, JP-5, Aviation Fuels, Supercritical Fuels, Fullerenes, Storage Stability

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Thermal Stability Enhancement of JP-5

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Work done under Navy Contract No. N68335-97-C-0324

For

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

1. EXECUTIVE SUMMARY

1.1. Background

In view of the ability of C_{60} to scavenge radicals, it was decided to test the effect it would have on oxidative thermal stability of jet fuels. In a preliminary study, conducted by SRI International in collaboration with the Naval Research Laboratory (NRL), it was found that doping fuels with 24 ppm of C_{60} had a significant beneficial effect in enhancing the thermal stability of a JP-5 and a diesel fuel, but only a marginal effect for a Jet A fuel. In the current study, the NRL provided Advanced Fuel Research, Inc. (AFR) and SRI samples of JP-5, Jet A, and diesel fuels to examine, by a variety of methods, the ability of pure C_{60} and its amine derivatives to influence thermal stability.

1.2. Experimental

Work was done at SRI to identify and/or synthesize fullerenes and fullerene derivatives that could be used as dopants to enhance fuel thermal stability. Chromatographically pure fullerene, C_{60}, was obtained from BuckyUSA Inc., TX. Two derivatives of C_{60} were prepared; both are adducts with alkyl amines—n-hexyl amine and di-isopropylamine. SRI refurbished a 1.2 liter Parr bomb reactor (316 stainless steel) sealed with a Teflon gasket for conducting oxygen-overpressure (OOP) tests. Tests were conducted by taking 50 mL fuel, with or without the additive, in a glass bottle, pressurizing the autoclave with 100 psig air, and heating the assembly in the oven of a gas chromatograph at 100°C for the specified period. The fullerene samples were also sent to the Air Force Wright Laboratories, where their efficacy was tested by Dr. Steve Andersen using a Jet-A fuel (No. 2827) under several standard procedures: Isothermal corrosion oxidation test, ICOT, (flask test, 180°C/5 h); quartz crystal microbalance, QCM, (140°C/15 h); and a hot liquid process simulator, HLPS, (a JFTOT-like test with a stainless steel tube and carbon-burnoff for assessing the amount of deposits; 260°C/5h). In the work done at AFR, a reactor system was constructed which was similar to the NRL gravimetric JFTOT experiment, but which also uses fiber optic infrared transmission cells to assess fuel thermal stability during thermal stressing at temperatures up to 500 °C and at a constant pressure of about 650 psig (FSTS).

1.3. Results & Discussion

The low temperature data from OOP, ICOT, QCM and HPLS tests show that C_{60} generally reduces the deposit formation, although the amount of reduction is only modest (between 5 and 30%). The two amine adducts tested in this study had a deleterious effect, except for JP-5 and diesel fuel in the OOP test. The beneficial effects seem to be larger under more severe conditions, as indicated by temperature or oxidation time (260°C JFTOT or 140°C QCM tests). The severity of the test can also be indicated by oxygen partial pressure. For example, the earlier OOP tests were done in oxygen instead of air and found a more beneficial effect of the C_{60} additive.

In the case of the FT-IR based FSTS, where the data were subjected to perturbation analysis for asymmetric wavelet transforms, the best improvements are observed in the medium temperature range (325 to 400 °C), which is consistent with the results for the other tests summarized above. When additional features of the FT-IR absorption spectra are considered (such as the OH region) the benefits are more pronounced in the highest temperature range (425-500 °C), although some potentially deleterious effects also appear to be enhanced at higher temperatures. The effects of reactor tube activation appeared to be important for this test, as the measured order of stability between the JP-5 and Jet A fuels reversed after tube activation.

5

1.4. Summary and Conclusions

In conclusion, it appears that the stability enhancing effects of pure C_{60} are manifest after the fuel has undergone some initial degradation. It is possible that the C_{60} promotes the formation of compounds which inhibit further oxidation. These effects can be more readily observed under moderate severity conditions. At very high severities, the C_{60} may catalyze or inhibit additional reactions, some of which are beneficial and some of which are deleterious. There appears to be no incentive to use amine derivatives of C_{60}. Additional work is warranted on exploring the beneficial temperature ranges which could still serve to extend the operating range of common jet fuels. The effects of surface activation in these systems needs further exploration.

2. INTRODUCTION

The formation of insolubles in the fuel is a general problem. It can happen under various conditions, such as thermal stressing of jet fuels at 250 - 400°C during a flight, or during long term (years) storage of diesels under ambient conditions (10 - 45°C). The formation of insoluble materials can lead to many problems such as plugging of filters or fouling of engine parts [1,2]. In the extreme case, when fuel flow is completely blocked, the consequence is extremely serious. Autoxidation has been implicated as a key step in the chemical scheme resulting in insolubles formation. This process involves generation of radical species, which initiate a chain reaction with oxygen to give oxidized hydrocarbons. The scheme, as originally proposed by Hazlett, is shown below:

INITIATION:

$$R\text{-}H \quad + \quad X \quad \rightarrow \quad R\bullet \quad + \quad XH$$

(metal ion or surface)

PROPAGATION:

$$R\bullet \quad + \quad O_2 \quad \rightarrow \quad ROO\bullet$$

$$ROO\bullet \quad + \quad R\text{-}H \quad \rightarrow \quad ROOH \quad + \quad R\bullet$$

TERMINATION:

$$ROO\bullet \quad + \quad ROO\bullet \quad \rightarrow \quad ROH \quad + \quad R'COR'' \quad + \quad O_2$$

$$ROO\bullet \quad + \quad R\bullet \quad \rightarrow \quad ROOR$$

$$R\bullet \quad + \quad R\bullet \quad \rightarrow \quad R\text{-}R$$
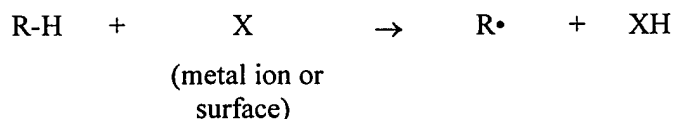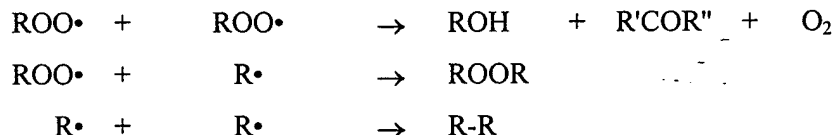
Numerous studies have been conducted on the chemistry leading to insolubles formation in jet fuels at elevated temperatures [1]. Key reactions are the thermal decomposition of alkyl chains by the Rice Herzfeld mechanism and autoxidation. In view of the ability of C_{60} to scavenge radicals [3], it was decided to test the effect it would have on (i) thermal stability of jet fuels, (ii) storage stability of diesels, and (iii) hydroperoxide formation. In a preliminary study, conducted by SRI in conjunction with the Naval Research Laboratory, is was found that doping the fuels with 24 ppm of C_{60} had a significant

beneficial effect in enhancing the thermal stability of jet fuels, but only a marginal effect for the storage stability of diesel fuels [4].

These tests were conducted using a gravimetric JFTOT apparatus at the NRL with a JP-5 fuel (J1) a commercial Jet A fuel (JA), and a diesel (J2). The JFTOT strip was heated to 260°C and 450 mL of fuel was pumped over it at 3.0 mL/min. The weight of the deposits on the strip, as well as those collected on the filter, were determined. The strip deposit was often very small (about 5-10%) of the total deposit. However, addition of 24 ppm C_{60} reduced deposit formation on the strip as well as the filtered deposit by about 50% for the J1 and J2 fuels. The data for the total deposits are displayed in Figure 1.

The reduction in the fuel J1, which had a commercial additive package in it, is particularly noteworthy, because C_{60} was able to further reduce the very small amount of the deposit. The diesel fuel (J2), which gave 15 mg/L of deposits, gave only 5.5 mg/L when doped with 24 ppm C_{60}. Finally, a commercial jet fuel, Jet A, which also had the additive package in it, showed no beneficial effect upon doping with C_{60}. The objective of the current study was to further investigate the use of fullerenes and fullerene derivatives as additives for improving the thermal stability of JP-5 and other fuels.

FUELS

J1: JP5 (contains additives)
J2: Diesel (unstable)
Jet A: Commercial aviation fuel (contains additives)

Doping at 24 mg/L
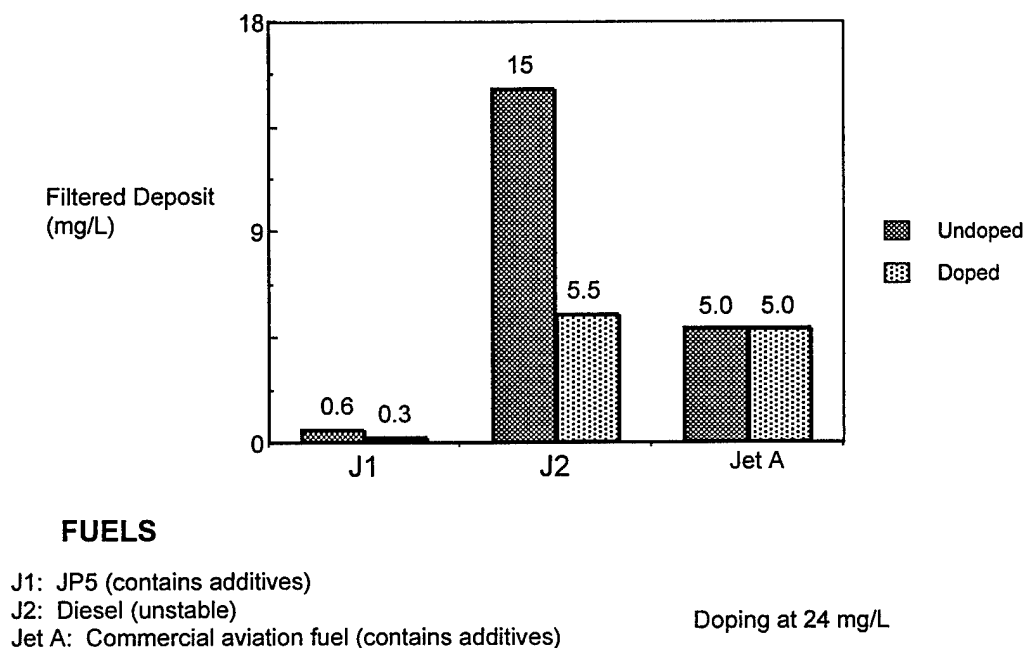
Figure 1. Effect of C_{60} on the thermal stability of fuels determined by using a gravimetric JFTOT [4].

3. MATERIALS

3.1. Selection of Fuel Samples

Discussions were held with the technical contract monitor, Dennis R. Hardy (DRH), concerning the selection of model fuels. It was decided that pure model fuels would be subjected to fairly limited testing in order to validate the methodology for a simple system. Another concern that was raised in the discussions with SRI was the solubility of fullerenes in some of the pure component fuels that were being considered. It was decided that DRH would provide to AFR and SRI samples of JP-5, Jet A, and diesel fuels and that these would be used for most of the work under Phase I.

3.2. Synthesis of Fullerenes and Fullerene Derivatives

Work was done at SRI to identify and/or synthesize fullerenes and fullerene derivatives that could be used as dopants to enhance fuel thermal stability. Chromatographically pure fullerene, C_{60}, was obtained from BuckyUSA Inc., TX. Two derivatives of C_{60} were prepared; both are adducts with alkyl amines— n-hexyl amine and di-isopropylamine. The adducts were prepared by the direct amination at low temperatures [5].

RR'NH

1. Benzene solution
2. freeze in liq. N_2
3. thaw

NRR'

Purple solution

Clear brown
solution

Typically 4 to 6 amine residues per C_{60}
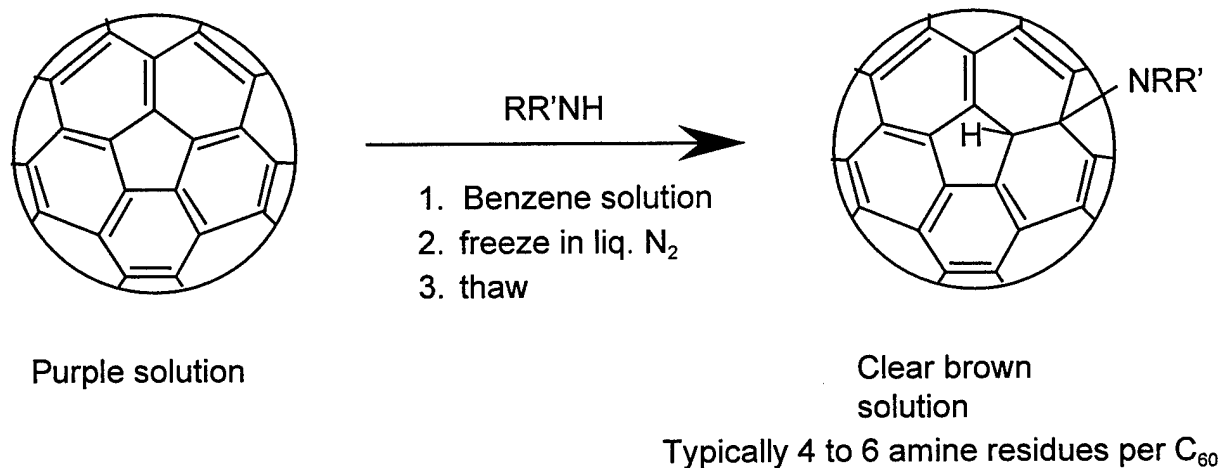
The additives were dissolved in toluene before adding to the fuel. The doping level in all tests was between 20 and 25 ppm. In order to account for the slight change in composition, an equivalent amount of toluene was added to the fuel in the control runs.

4. THERMAL STRESSING EXPERIMENTS

4.1. SRI Static Tests

SRI refurbished a 1.2 liter Parr bomb reactor (316 stainless steel) sealed with a Teflon gasket that is rated to 1900 psi at 300°C. This reactor has a 4-in. i.d. and a 5.37-in. height, and it can accept four 80 ml bottles. The exact procedures for conducting the oxygen-overpressure (OOP) test for determining the thermal stability of jet fuels were reviewed in consultation with personnel from the NRL. The reactor was tested for leaks and found to be leak proof.

Since the autoclave could hold four 80 -mL bottles, two tests (with two controls) were run in parallel. Tests were conducted by taking 50 mL fuel, with or without the additive, in a glass bottle, pressurizing the autoclave with 100 psig air, and heating the assembly in the oven of a gas chromatograph at 100°C for the specified period. The temperature was monitored by a thermocouple attached directly to the reactor wall. At the end of the test, the fuel and the control was filtered through a tared nylon membrane filter (0.2 μm), which was dried and reweighed to determine the amount of the the insolubles. Because the amount of the deposits was very small, the weighings were performed by using an electronic balance capable of reading with an accuracy of ± 0.01 mg.

4.2. Air Force Experiments

The fullerene samples were also sent to the Air Force Wright Laboratories, where their efficacy was tested by Dr. Steve Andersen using a Jet-A fuel (No. 2827) under several standard procedures: Isothermal corrosion oxidation test, ICOT, (flask test, 180°C/5 h); quartz crystal microbalance, QCM, (140°C/15 h); and a hot liquid process simulator, HLPS, (a JFTOT-like test with a stainless steel tube and carbon-burnoff for assessing the amount of deposits; 260°C/5h).

## 4.3. AFR Fuel Stability Test System

A reactor system was previously developed under contracts with the Air Force which uses infrared spectroscopy measurements to assess fuel thermal stability during thermal stressing [6]. The system utilizes fiber optic infrared transmission cells and can make direct measurements of oxygenated species, as shown in Figure 2, and deposit forming tendencies, as shown in Figure 3. Since the system had not been used for three years and had been dismantled, the redesign, re-construction and testing of the reactor and optical system was carried out in the early stages the Phase I program.

In this system, fuel is delivered via a high-pressure pump to a ¼" ID and 8" long electrically heated stainless steel reactor tube followed by an IR cell assembly. A schematic diagram of the entire system is shown in Figure 4. An inline metallic 1 micron filter was also incorporated into the system. The function of this filter was to provide large metallic surfaces for the particles to deposit or coalesce. The pressure is kept constant at 650 psig for each condition via a backpressure regulator mounted at the end of the reactor assembly. The transmission cell consists of a 1/16" cross with polished chalcogenide fibers installed in opposed ports as shown in Figure 5a. The fiber was encased into 1/16" stainless steel tubes using epoxy polymer glue, as shown in Figure 5b. This allowed using standard stainless steel ferrules to create a high pressure seal. Adjusting the gap between the two fibers controls the optical pathlength of the transmission cell. The gap in the present setup is 500 microns. A DTGS infrared detector was mounted on the assembly with the output fiber positioned directly adjacent to the detector element.

5. RESULTS AND DISCUSSION

5.1. SRI Static Tests

The chemistry of insolubles formation during long term storage is fairly complex and involves many different reactions. A possible scenario includes oxidation of sulfur species to sulfonic acids which catalyze the nucleophilic reaction of alkylindoles with phenalenones, which are also formed by autoxidation [7]. The storage stability of diesels is best determined by the oxygen over pressure (OOP) test developed at the Naval Research Laboratory [8]. In a preliminary study [4], we had used this test to see if C_{60} can prevent insolubles formation in two diesel fuels (D1 and D2). Both of the fuels were a 20% light cycle oil blend with the straight run diesel. The fuels were stressed for 16 h at 90°C with 100 psig O_2. The results, shown in Table 1, indicate that, at the doping level of 24 ppm, both fuels responded to the addition of C_{60}, although the more unstable fuel, Fuel D1, exhibited a modest 16% reduction deposit formation. At a similar level of doping with an alkyl amine additive, these fuels showed a reduction in deposit formation of about 70%. Thus, pure C_{60} was not a particularly effective agent for enhancing the storage stability of these diesel fuels.

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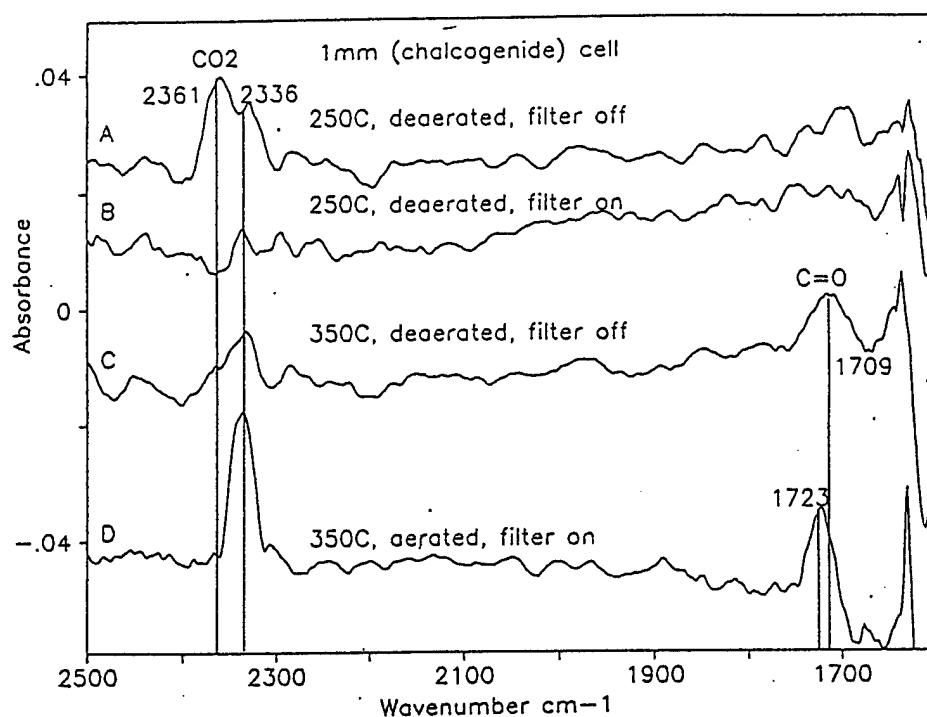
Figure 2. (a,b,c) Absorbance spectra obtained during thermal stressing of deaerated Sun jet fuel showing the formation of carbon dioxide and carboxylic acids and d) absorbance spectrum obtained during thermal stressing of an aerated Sun jet fuel showing the formation of carbon dioxide and ketones [6].
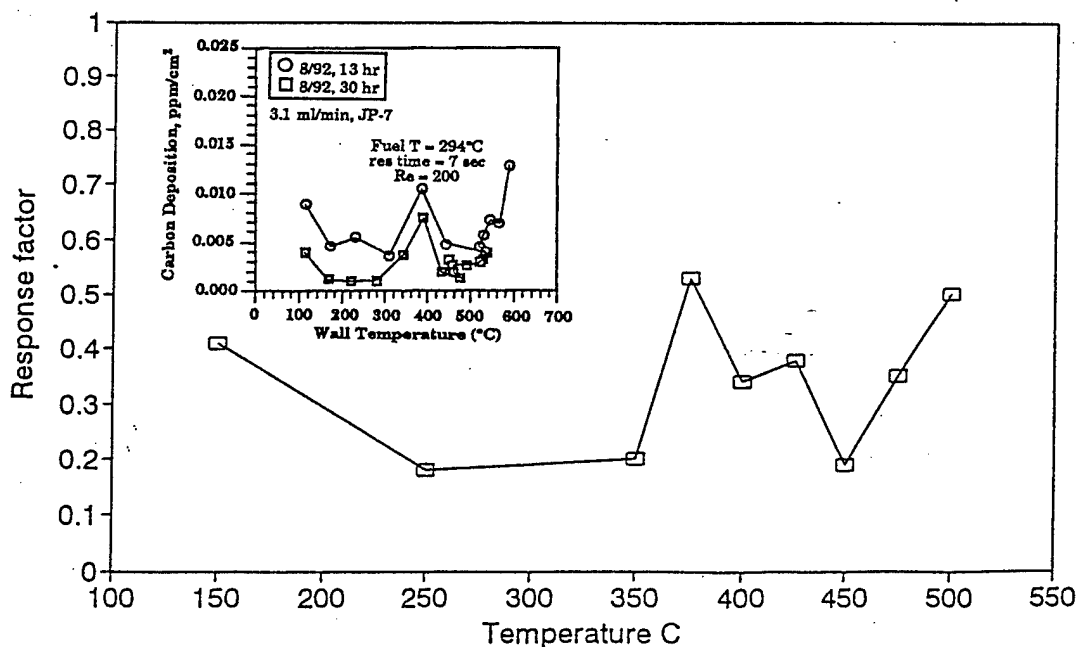
Figure 3. Differential spectral response (filter off - filter on) results from small gap cell and C-H deformation region for thermal stressing experiments with aerated Shell fuel compared with results of Edwards and Zabarnick (1993) for JP-7 fuel under similar conditions (inset) [6].

10
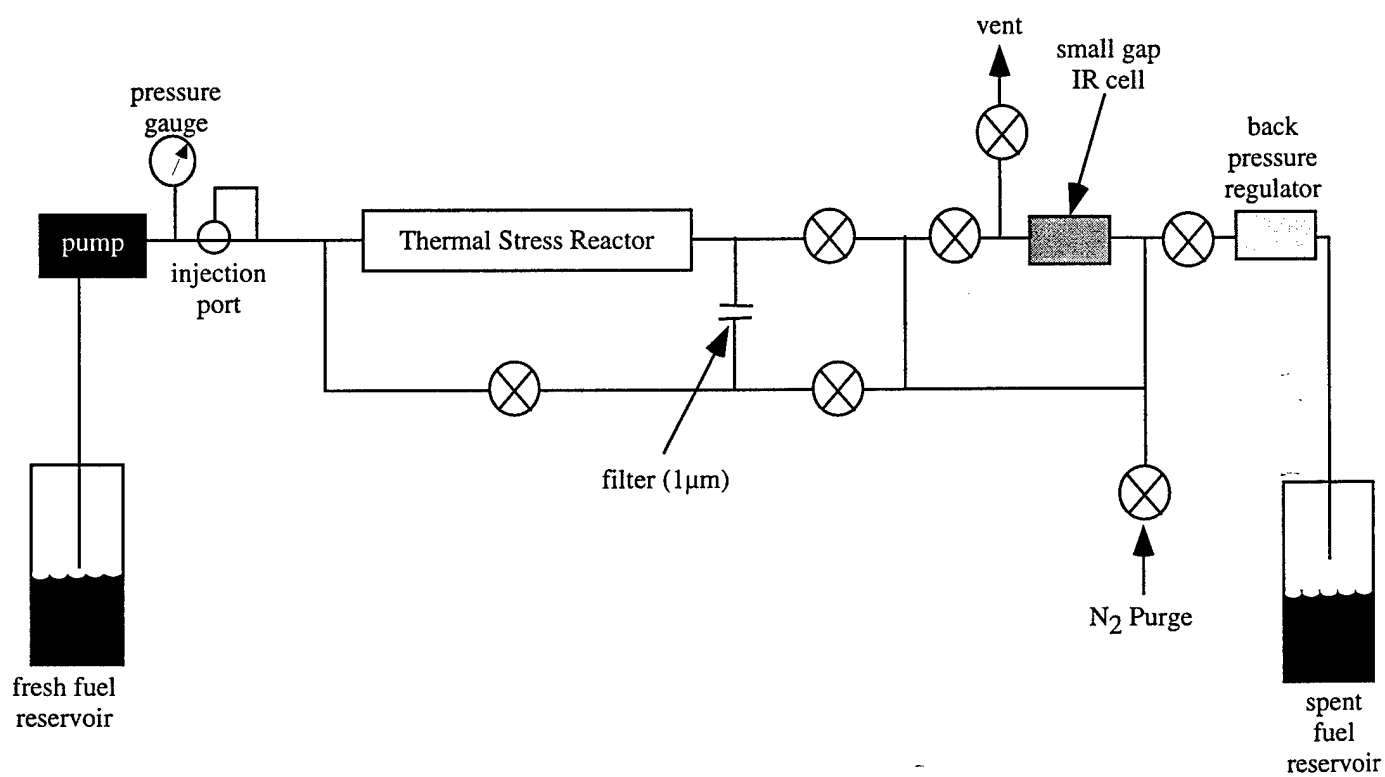
Figure 4. Block diagram of the system to carry out thermal stressing of fuel.

a *Transmittance Cell-Side View*

Fuel

Focussed IR Light

High Pressure Transmission Cell

Preamplifier

Adjustable Gap

DTGS Detector
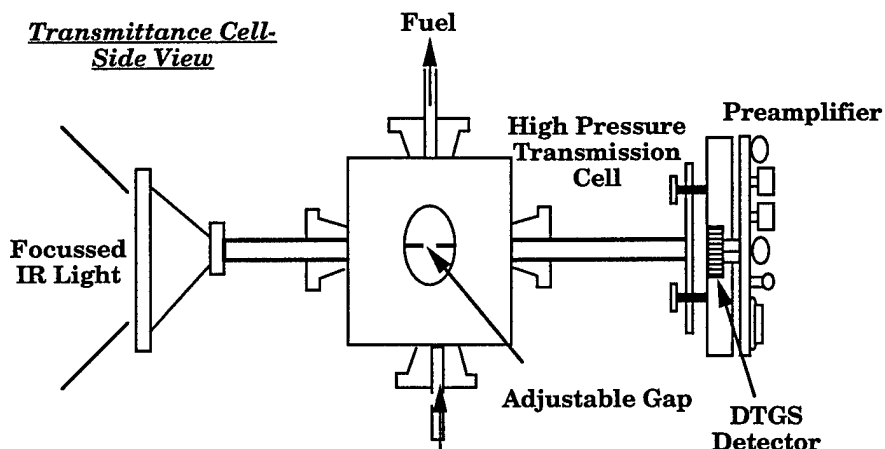
b *Design of Fiber Element*

1"

1/16" stainless steel tube

Epoxy

Cladding

IR Beam

Fiber

Distance to Determine Gap

1/16 "Swagelock Ferrule
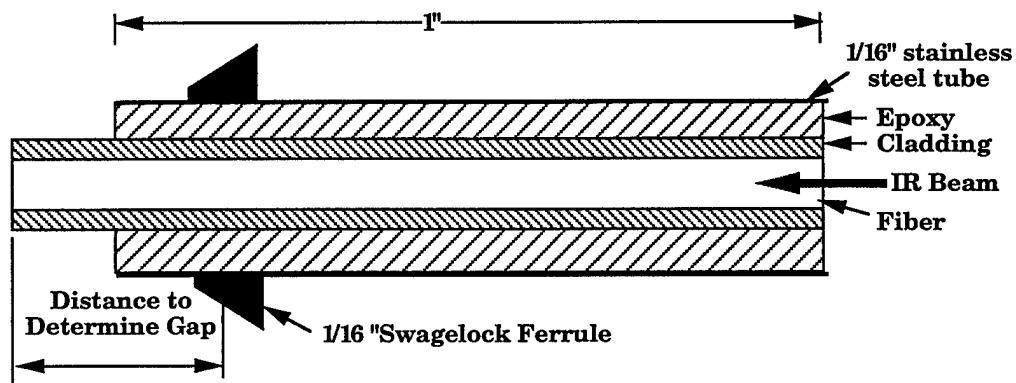
Figure 5. The High Pressure Fiber Optic Transmission Cell Consists of a 1/16" Cross with Polished Fibers Installed in Opposed Ports. The Optical Pathlength of the Transmission Cell is Controlled by Adjusting the Gap Between the Two Fibers. Several Combinations of Cell Pathlength, Fiber Material, and Detector Type can be Selected Depending Upon the Type of Measurements that is Desired.

Table 1. Effect of C_{60} on the insolubles formation (mg/ℓ) in diesel fuels during the oxygen overpressure test (90°C, 16 h, 100 psig O_2) [4].

Fuel ID	Neat	+24 ppm C_{60}	% Redn.
DI	56	47	16
D2	44	34	23

For the present study, we used a variation of the OOP test for assessing the efficacy of three jet fuels and a diesel fuel. The results from these tests are shown in Table 2. The data show that C_{60} consistently reduces the deposit formation, although the amount of reduction is modest. The hexylamine adduct reduced deposit formation in JP-5 and the diesel fuel, but had a deleterious effect in Jet A and JP-8.

Table 2. Effect of C_{60} and its hexylamine adduct on the storage stability of jet and diesel fuels (100°C, 100 h, 100 psig air)

Insoluble Products, mg/ℓ

Fuel	Neat	+ C_{60}	+ C_{60}-hxNH$_2$
Jet A	20.6	19.8	
	19.4		23.4
JP-5	31.4	30.2	
	29.8		24.6
JP-8	16.6	15.6	
	8.6		11.2
Diesel	300.1	290.2	
	310.8		298.4

additive: 20 ppm

5.2 Air Force Experiments

During this program, we sent samples of C_{60} and its amine adducts to the Wright Air Force Laboratory, where several tests were conducted, as discussed in section 4.2. The results, given in Table 3, show that while C_{60} has a small (10 to 30%) but consistent beneficial effect, the amine adducts appear to increase the deposits. The reduction of deposits for pure C_{60} was 10% in the ICOT test, but about 30% in the QCM test, which is conducted at a higher temperature.

Table 3. Effect of C_{60} and its amine adducts on the thermal stability of a jet fuel (2827)

Additive	ICOT (mg/mL)	QCM (mg/cm^2)	HLPS (mg/cm^2, ΔP)
None	45	2.5	70, 300/150
C_{60}	41	1.8	64, > 300/165
C_{60}-hexylamine adduct	70	3.4	-
C_{60}-disopropylamine adduct	59	2.3	-

ICOT: Isothermal Corrosion-Oxidation Test (Flask Test, 180°C/5 h)
QCM: Quartz Crystal Microbalance (140°C/15 h)
HLPS: Hot Liquid Process Simulator (JFTOT-like, SS tube, carbon burnoff, 260°C/5 h)

5.3. AFR Fuel Stability Test System (FSTS) Experiments

Methodology Development - The redesigned and reconstructed Fuel Stability Test System (FSTS), described above, was initially tested on some fuels that were on hand at AFR from previous projects. In earlier work, done for the Wright Aeronautical Laboratories, this system was used to determine the presence of trace oxygenated species (CO_2, carboxylic acids, ketones) and particulate matter from the thermal degradation of jet fuels [6]. Examples of these data are shown in Figures 2 and 3. In the case of particulate measurements, the idea is to measure characteristic changes related to particulate formation rather than measurements of functional group concentrations. This allows for collection of data which is relatively independent of fuel chemical composition.

Preliminary tests of the system were carried out with SUN Jet A-1 and UN1863 fuels to establish the best testing protocol. A constant flow of 1 cc/min was maintained during the experiments and IR spectra were collected at the particular test temperature with the inline filter connected (filter on) and with the filter bypassed (filter off). The spectra were collected after equilibrium conditions were reached, which was typically 10-15 minutes. The reference spectrum was the room temperature spectrum with the filter on condition.

Figures 6 and 7 demonstrate the characteristic IR absorbance data for various test conditions. The 1540-1300 cm^{-1} wavelength region of aliphatic deformation modes was found to be a good indicator of particulate behavior. This is because the fuels are significantly aliphatic in nature. The aliphatic vibrational modes around 2500 cm^{-1} could not be used in this study because of the near saturation of the bands. Since the spectra are referenced to the room temperature spectrum of the same fuel, the spectra shown in Figures 6 and 7 depict changes as a result of thermal stress. S or multiple S shaped features, as seen on Figures 6 and 7 with both positive and negative lobes, typically occur as a result of band shifts and/or intensity changes.

The assumption was that the comparison of filter-off to filter-on responses at any given temperature is characteristic of the particulate concentration, particle size and/or tendency to form deposits. Therefore, it is useful to see how the filter-off / filter-on ratio of the integral of the positive (P') and negative (N') parts of the "S" lobes of the features around 1450 cm^{-1} change with temperature. This is shown in Figures 8 and 9 for the two fuels tested and it is seen that, in the 250-350 °C region, the values of both P' and N' deviate from unity. It is also seen that, although the particular deviations from unity do not seem to follow a simple or "smooth" function, the deviations at a particular temperature between 250 °C and 350 °C are always opposite for P' as compared to N'. In other words, the "placement" of the S deviations above or below the spectral baseline might not be a good representation of this phenomenon. The sum or difference of the negative and positive integrals turned out to be a better representation. Figure 10 shows the difference of the integral ratios, ABS (P'-N'), for the two fuels. It is seen that the well-known maximum tendency of deposit formation in the 300 °C region is clearly observable with both fuels.

In order to meet the objectives of the current project, the system shown in Figure 4 was modified to approximate the conditions in the gravimetric JFTOT apparatus developed by Hardy et al. [9]. This was done in order to provide quantitative as well as qualitative measurements of the effects of the dopants on fuel thermal stability in a flow system. A 21 inch long ¼" O.D. titanium tube with a stainless steel wire insert was used to stress the fuel (volume: 8.5cc; flow rate 0.5cc/min; residence time: ~17 min). This was done to allow collection of measurable quantities of deposits. The titanium is considered less active than stainless steel towards surface catalyzed reactions. In addition, the effluent was filtered through a 0.2-micron filter.

While waiting for the new fuel samples to be received (new JP-5, Jet-A and diesel fuel), an older (around 10 years old) JP-5 fuel sample was also tested in the reactor using the on-line FT-IR method, as described above, and the data (in comparison with the SUN data) are shown in Figure 11. These data were analyzed using the method described in regard to Figure 10 (see Table 4, "old method"). Although the peak around 400°C, which we consider to correspond to high temperature deposit formation, starts somewhat later with the more stable JP-5, the actual numbers were significantly higher with JP-5 than with the supposedly less stable SUN fuel. This indicated that the "asymmetry" of the filter-on/filter-off difference of the original spectra might not necessarily be adequate for quantitative assessment. It was thought that the significant noise level of the original spectra could be responsible for this discrepancy. Applying advanced digital filtering to carry out noise removal supported this conclusion. Figure 12 shows the data calculated from spectra modified using wavelet analyses techniques for noise removal and analyzed using the "improved method" outlined in Table 4. It is seen that, in this case, the actual numbers are of the same range for the two fuels. A further enhancement to the wavelet technique was made by using something known as a "two channel perfect reconstruction technique." In this case, one channel goes through a low pass filter and the other channel goes through a high pass filter. Normally the two channels are reconstructed to give back the original spectrum. However, it was found that using only the spectrum that goes through the low pass filter provided better noise rejection. This technique is included in Table 4 as the "best method."
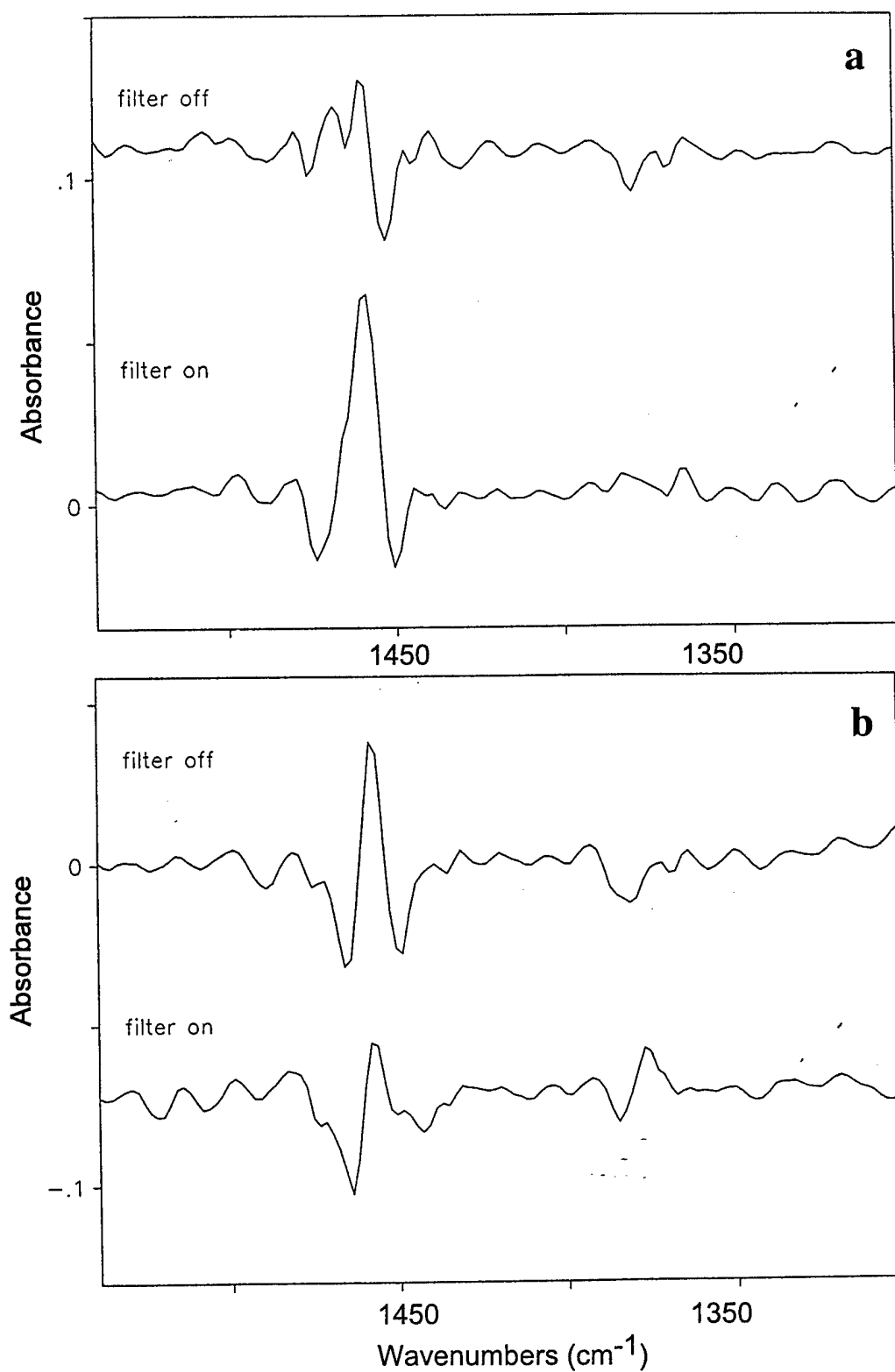
Figure 6. IR absorbance spectra for Sun fuel at a) 275°C and b) 300°C (referred to room temperature, filter on condition).
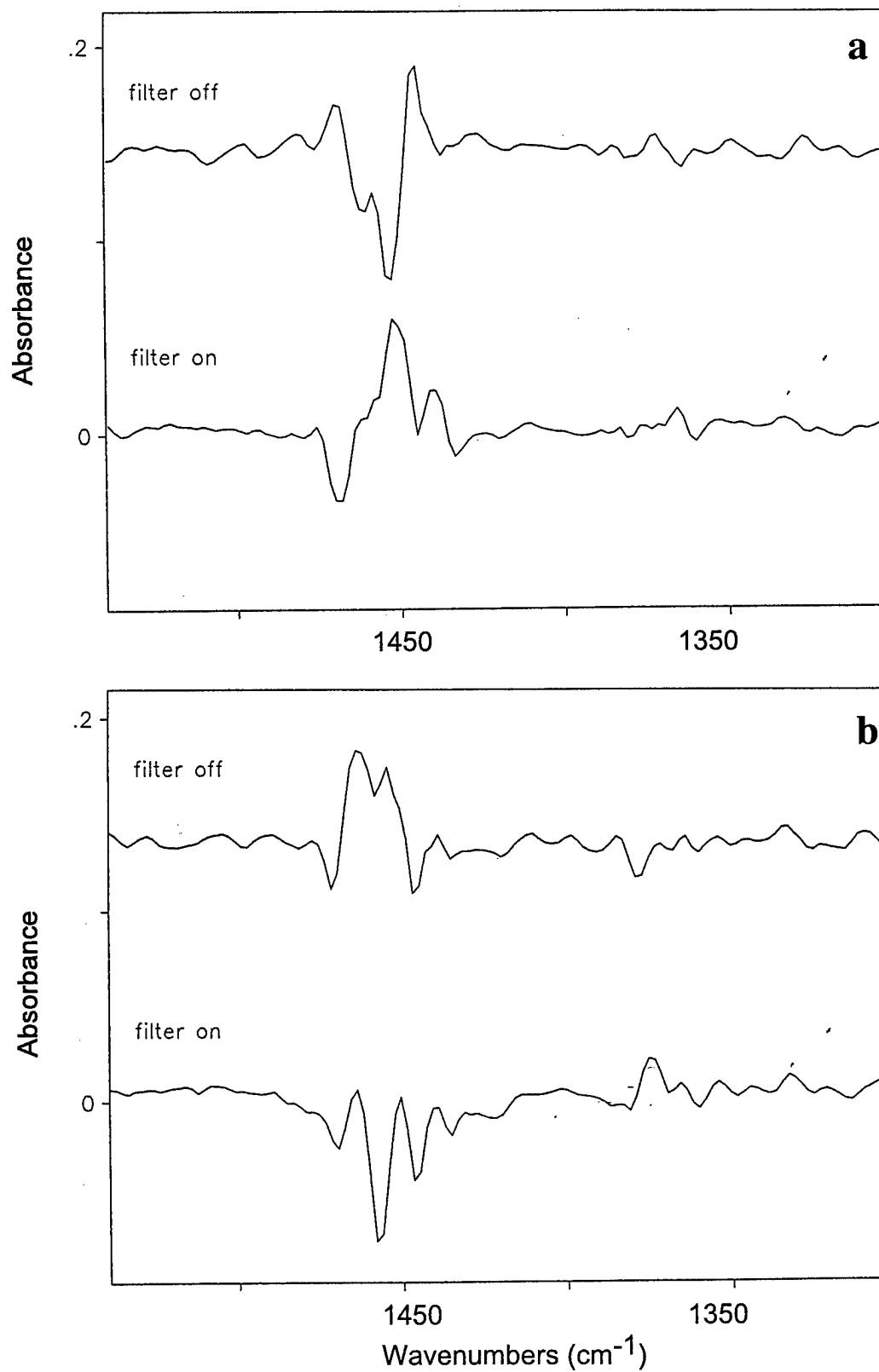
Figure 7. IR absorbance spectra for UN1863 fuel at a) 250°C and b) 275°C (referred to room temperature, filter on condition).

17
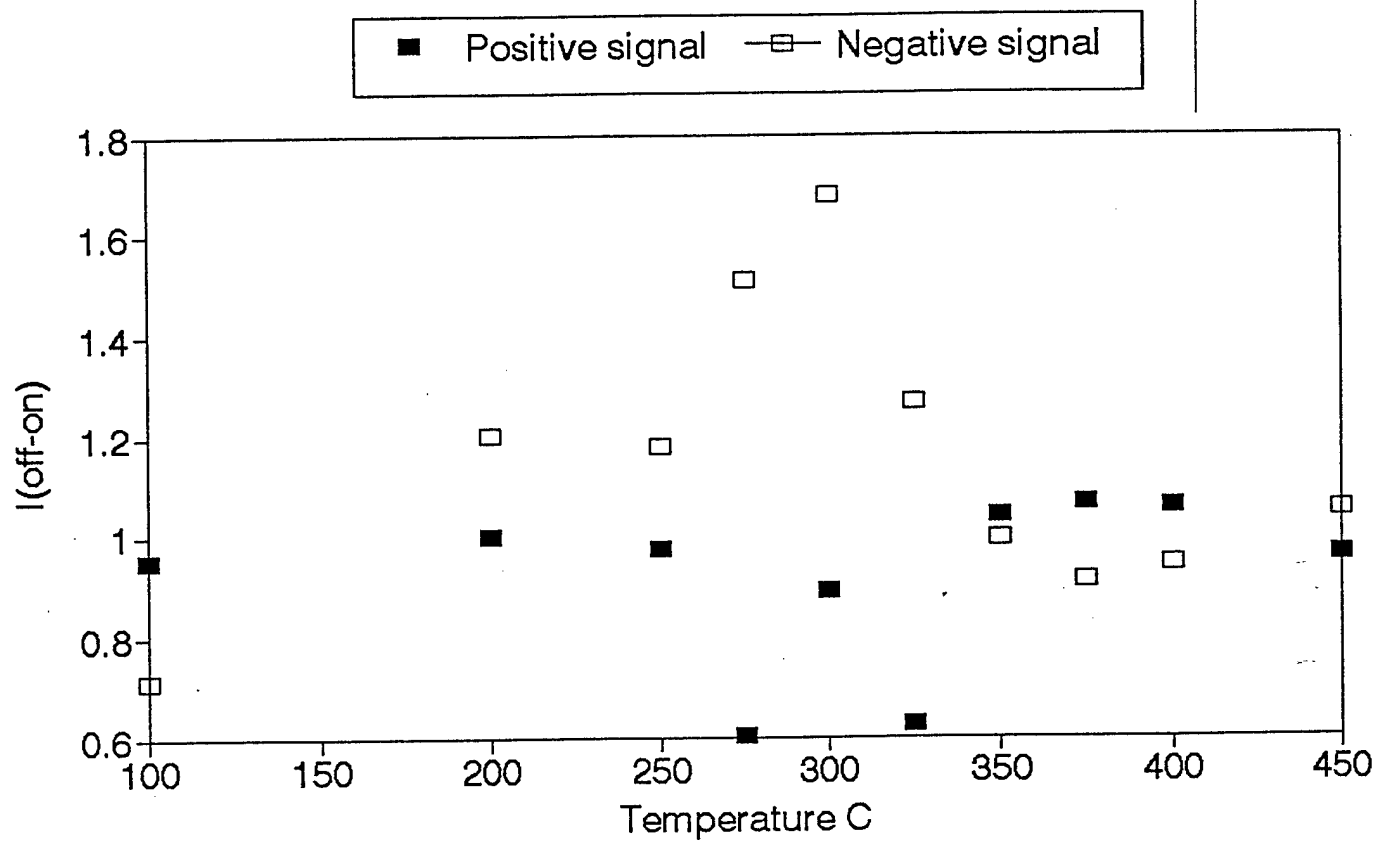
Figure 8. Filter off / filter on response ratio of the integrals of the positive and negative absorbance features around 1450 cm^{-1} as a function of temperature for Sun fuel.
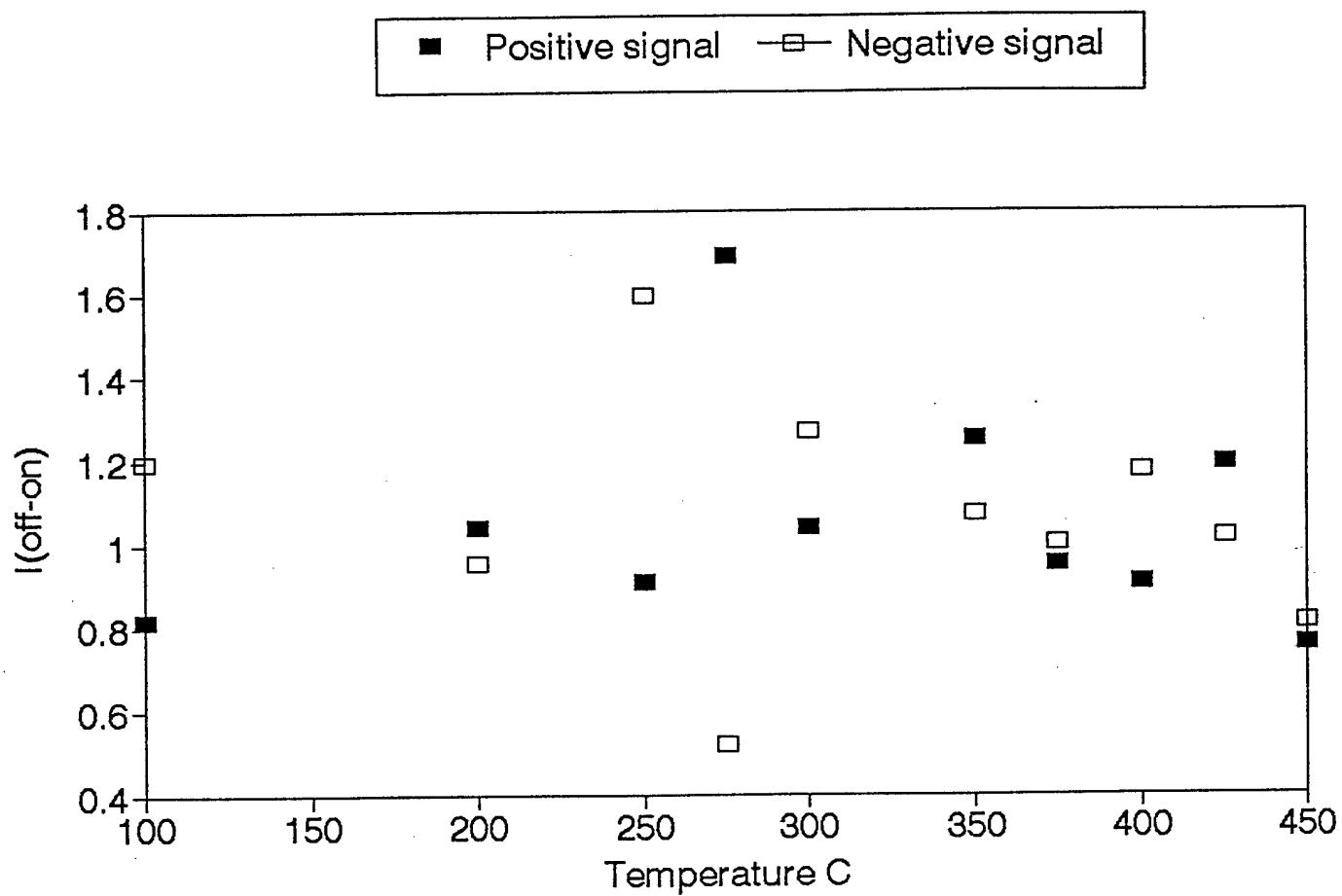
Figure 9. Filter off / filter on response ratio of the integrals of the positive and negative absorbance features around 1450 cm^{-1} as a function of temperature for UN1863 fuel.
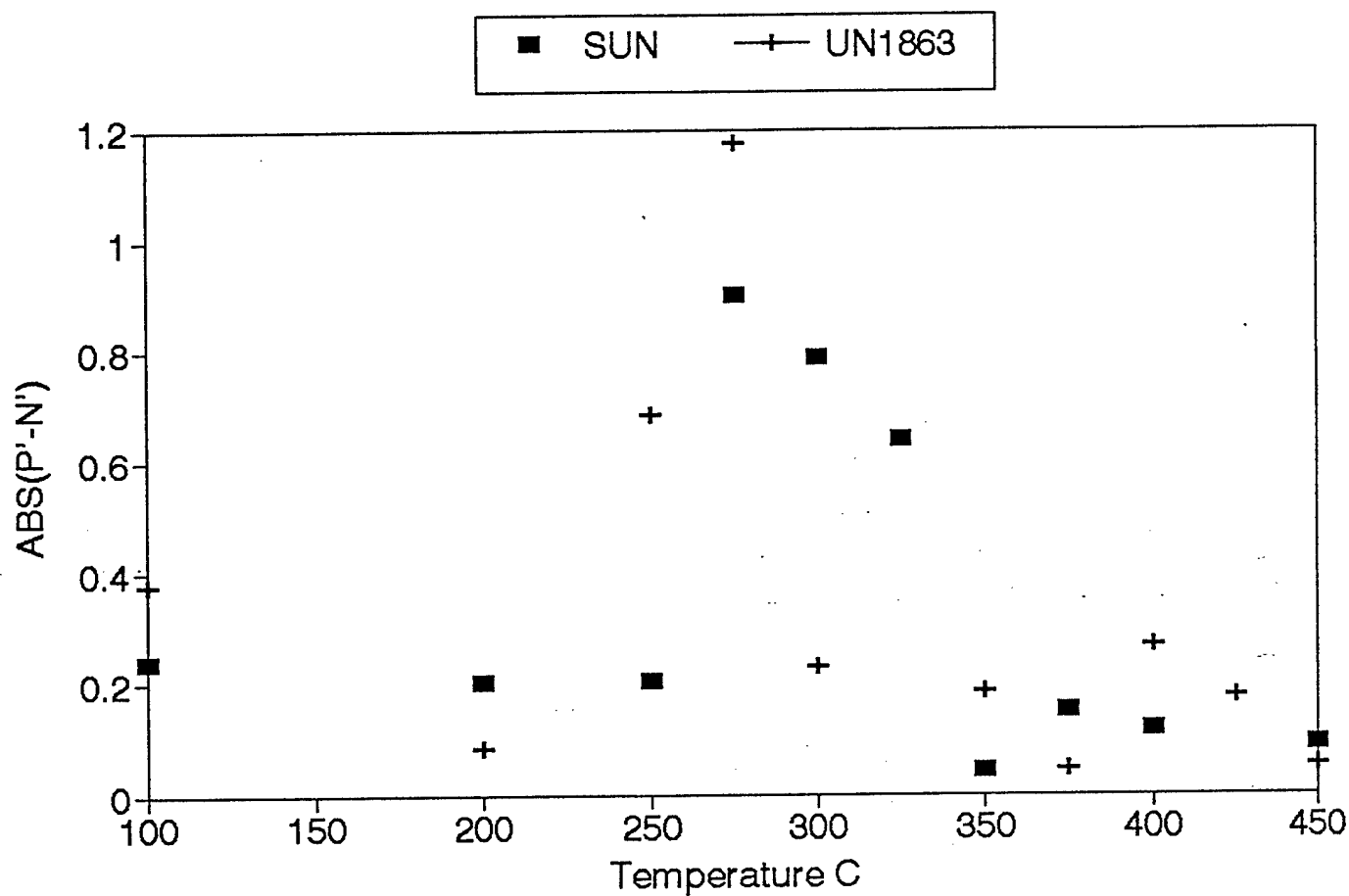
Figure 10. Absolute value of the difference of the integrals of the positive and negative absorbance features around 1450 cm-1 as a function of temperature for Sun and UN1863 fuels.
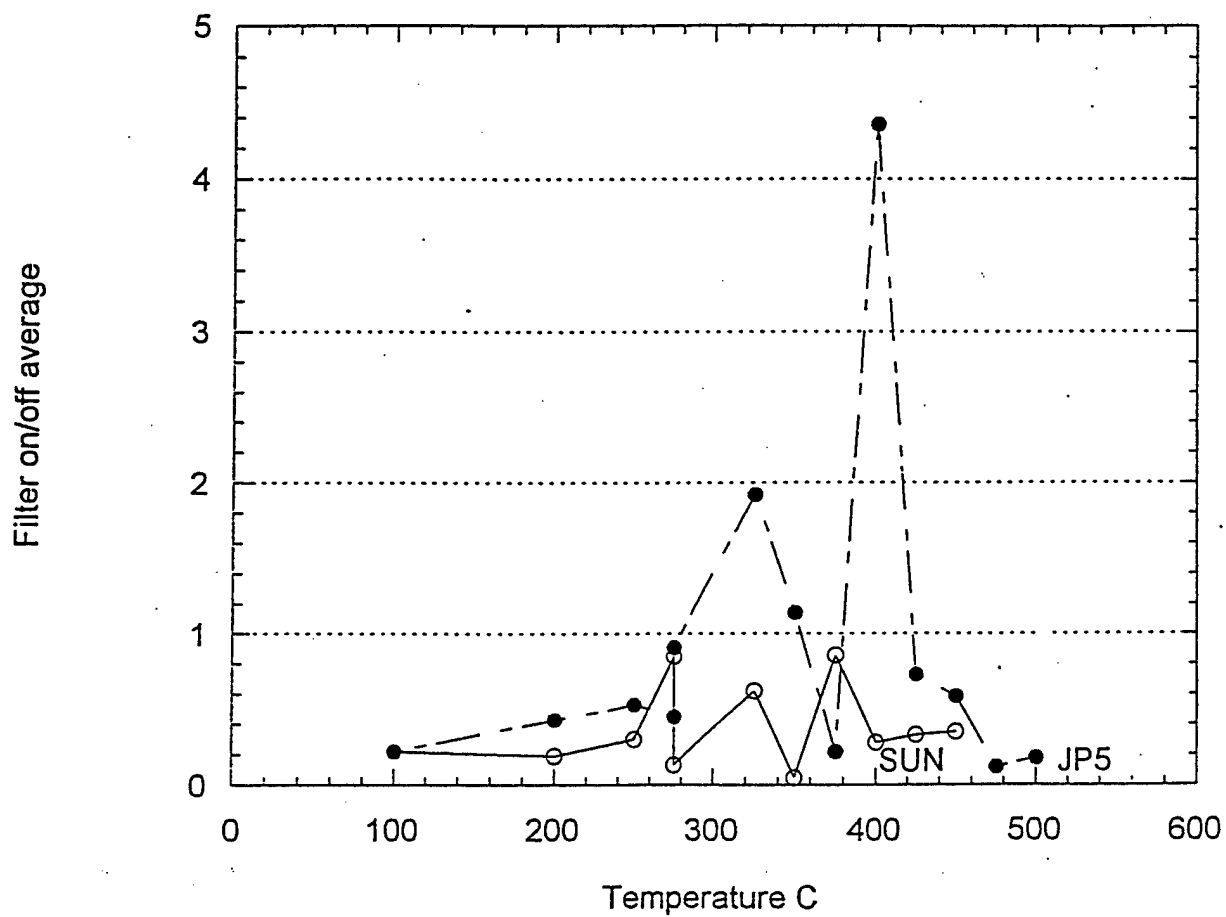
Figure 11. Filter on- filter off response (average of several runs) calculated using old method (see Table 1) for SUN and old JP-5 fuels stressed over a range of temperatures.
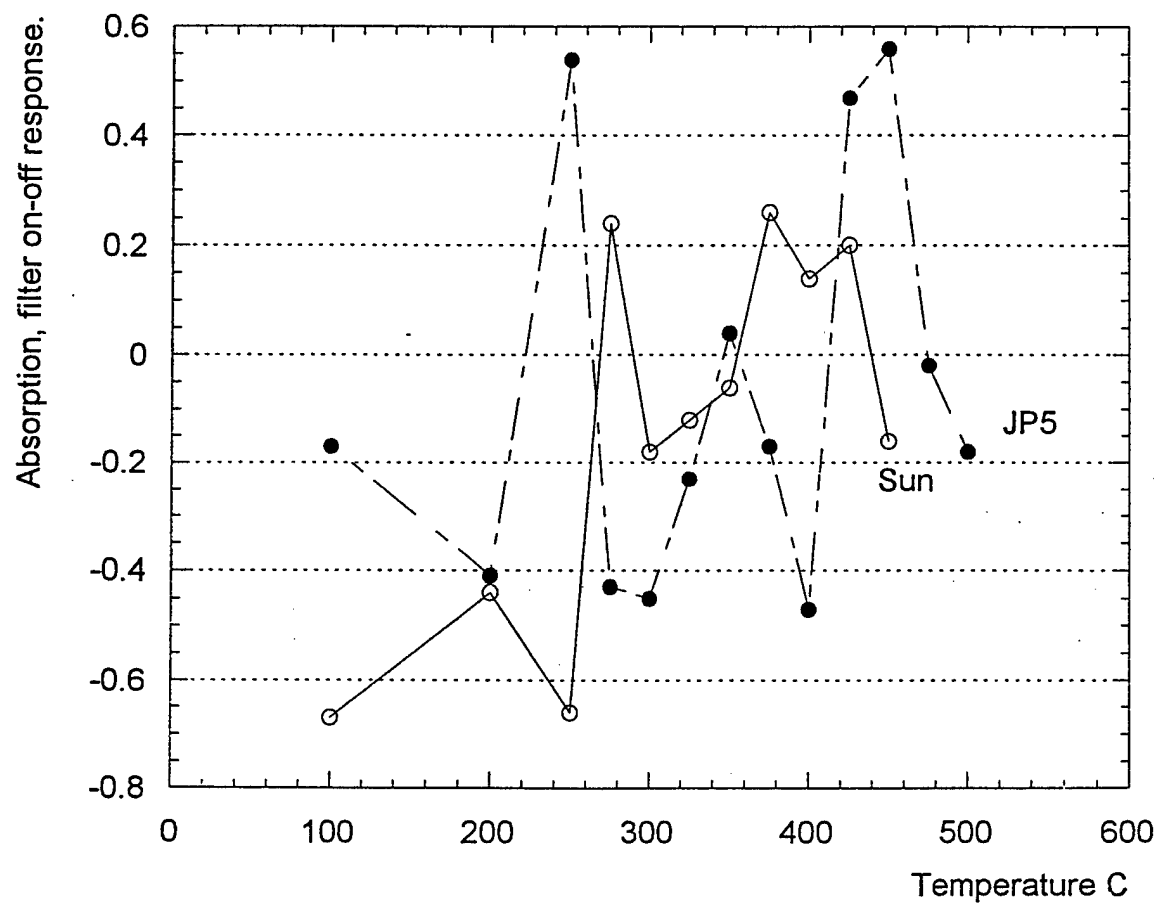
Figure 12. Filter on- filter off response calculated using improved wavelet filtering method (see Table 4) for SUN and old JP-5 fuels stressed over a range of temperatures.

Figure 13 shows the perturbation results using the "best method" for the new JP-5 sample received from NRL as measured in the modified reactor system, which is more stable than the old Jet A and diesel samples, as expected. Figure 14 shows the same comparison, with a different set of wavelet parameters which show an enhanced deposit forming tendency for the diesel fuel. The wavelet parameter set used to process the data shown in Figure 13 (No. 3) is best for showing fine differences between fuels, while the parameter set used to generate Figure 14 is best for showing gross differences between fuels. The FT-IR data for the studies on C_{60} additives were analyzed using parameter set no. 3 and the results are given in Tables 5 and 7.

**Table 4 – Perturbation analysis of on-line FT-IR transmission spectra of stressed fuels to obtain information on deposition rates**

Old Method (Figs. 10 & 11)	Improved Method (Fig. 12)	Best Method (Figs. 13,14; Tables 5,7)
1. Normalize spectra to room temp.	Normalize spectra to room temp.	Normalize spectra to room temp.
2. Integrate positive and negative features separately	Integrate positive and negative features separately	Take absolute value of (filter on – filter off)
3. Calculate absolute value of difference between positive and negative features	Smooth spectral data using wavelet analysis	Use bias spectra (low pass filter)
4. (filter on – filter off)	Integrate positive and negative features	Use integral of absolute values

Effects of Reactor Tube Activation – Before addressing the effects of C_{60} additives on fuel thermal stability, the effects of reactor tube activation also needs to be considered. Reactor tube activation is defined by the observation of increased thermal degradation of the fuel during repeat trials of the same fuel under the same nominal conditions. The activation of the reactor tube might have been the result of either thermal stressing of an unstable fuel (diesel fuel) and/or thermal stressing of a jet fuel in the presence of C_{60}. There is a possibility that the thermal decomposition of the unstable diesel fuel resulted in a lacquered surface of the reactor tube. It was shown in the literature that this increased the decomposition rate of jet fuels [10]. The FT-IR perturbation analysis data based on wavelet filtering are shown in Table 5. While before the activation, Jet A fuel was more stable than JP-5, after the activation JP-5 was the more stable, based on the IR perturbation criteria. In addition, the activated reactor tube resulted in significantly larger perturbation values with both fuels. The data on the amounts of filterable materials are shown in Table 6. Significantly more material could be filtered out before the activation than it could be filtered out after the activation took place. However, in both cases, the amounts of filtered products are very small, and it is not clear that any firm conclusions can be drawn from this data.
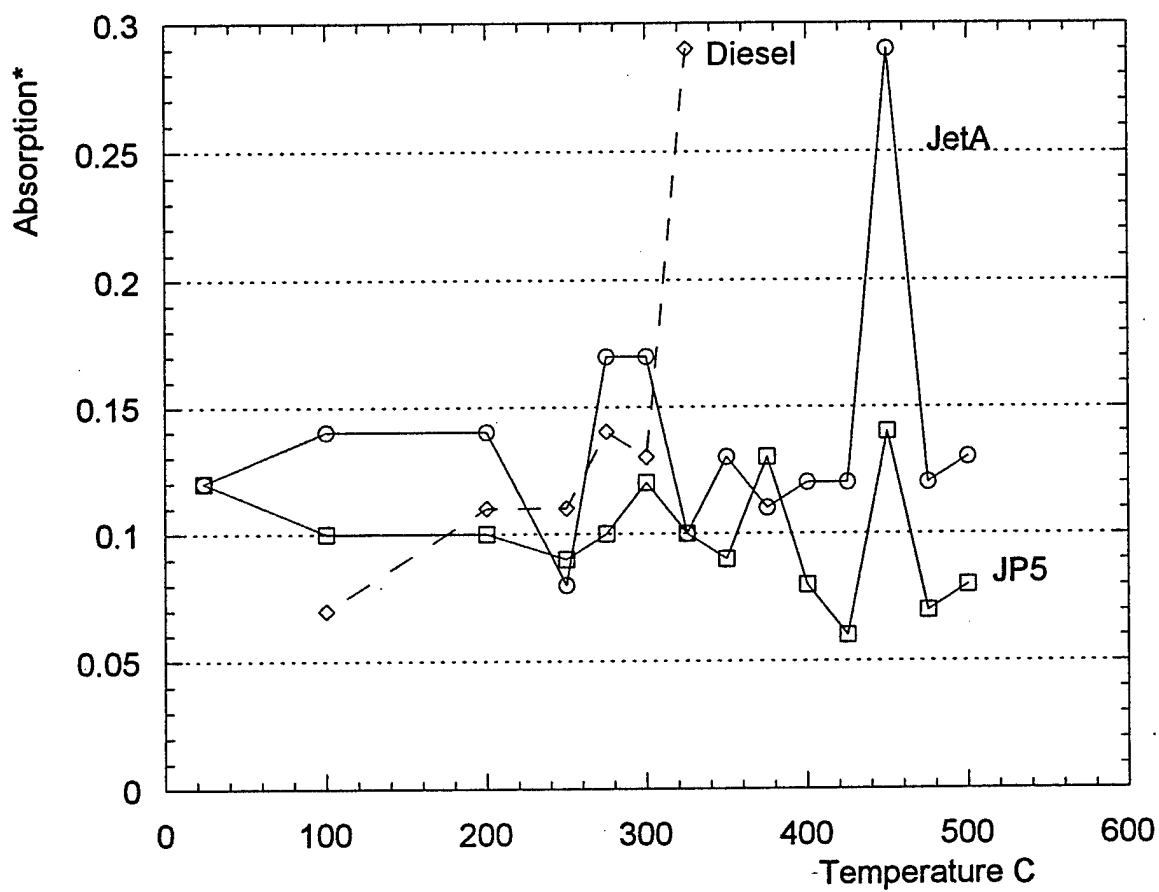
Figure 13. Integral of absolute values of absorption between 1300 - 1540 cm^{-1}. Filter on referenced to filter off at a given temperature. Data analysis done using wavelet filters, parameter set no. 3.

24
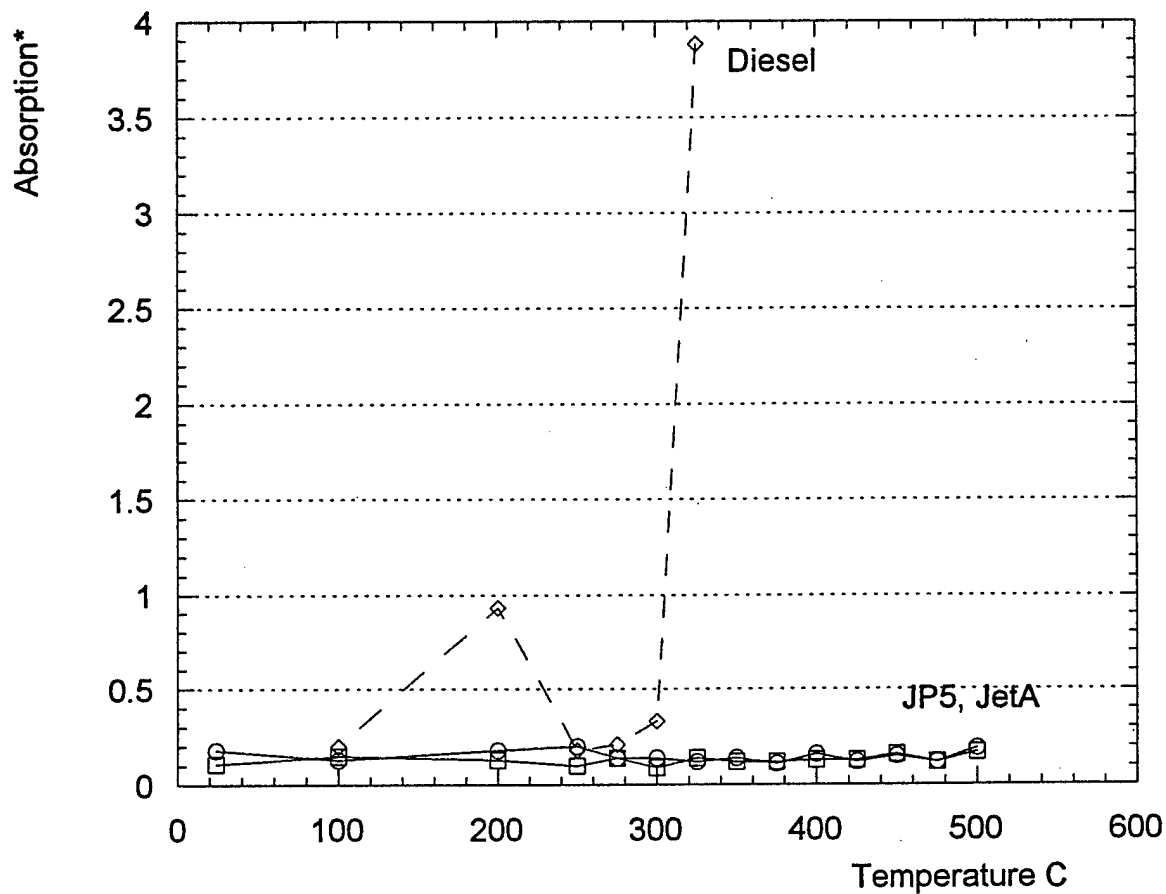
Figure 14. Integral of absolute values of absorption between 1300 - 1540 cm^{-1}. Filter on referenced to filter off at a given temperature. Data analysis done using wavelet filters, parameter set no. 4.

Table 5 - FTIR perturbation data (arbitrary units) based on asymmetric wavelet transforms

Temp.	Before activation		After Activation								
°C	JP-5	JetA	Diesel	JP-5	JP+ toluene	JP-5+C_{60}	JP-5+C_{60} repeat	JP-5+C_{60} modif.	JetA	JetA+C_{60}	JetA+C_{60} repeat
24	0.12	0.12	0.19	0.11	0.26	0.23	0.23	0.15	0.22	0.24	0.19
100	0.14	0.1	0.92	0.23	0.28	0.18	0.17	0.18	0.25	0.17	0.16
200	0.14	0.1	0.23	0.17	0.21	0.21	0.16	0.21	0.24	0.27	0.16
250	0.08	0.08	0.21	0.25	0.18	0.2	0.22	0.22	0.24	0.33	0.17
275	0.17	0.1	0.33	0.25	0.2	0.26	0.33	0.23	0.24	0.26	0.23
300	0.17	0.12	3.79	0.18	0.2	0.2	0.28	0.75	0.25	0.31	0.3
325	0.1	0.1	sat.	0.25	0.23	0.17	0.28	0.17	0.28	0.22	0.26
350	0.13	0.09	sat.	0.25	0.21	0.16	0.22	0.18	0.2	0.23	0.24
375	0.11	0.13	sat.	0.17	0.23	0.23	0.21	0.17	0.26	0.25	0.25
400	0.12	0.08	sat.	0.22	0.23	0.17	0.21	0.21	0.2	0.16	0.2
425	0.12	0.06	sat.	0.2	0.19	0.23	0.25	0.19	0.29	0.23	0.31
450	0.29	0.14	sat.	0.32	0.13	0.18	0.23	0.26	0.32	0.26	0.24
475	0.12	0.07	sat.	0.23	0.17	0.17	0.25	0.23	0.21	0.19	0.22
500	0.13	0.08	sat.	0.25	0.22	0.23	0.23	0.18	0.2	0.18	0.23

Notes: sat = values too high, above saturation level of instrument

Table 6 – Amounts of filtrate collected from 0.2μm filter*

Temp. °C	Before	After reactor tube activation				
	JP-5	JP-5	JP-5+ toluene	JP-5+C_{60}	JP-5+C_{60} modif.	JetA+C_{60}
24	0.07	0.01				
100	0.08	0.02				
200	0.06	0.02				
250	0.07	0.02	0.01	0.02	0.01	0.01
275	0.05	0.01	0.05	0.03		
300	0.07	0.04	0.04	0.02	0.01	0.01
325	0.06	0.02	0.04	0.01	0.01	0.01
350	0.04	0.01	0.02	0.02	0.02	0.01
375	0.03	0.01	0.01	0.03	0.01	0.01
400	0.04	0.02	0.01	0.05	0.03	0.03
425	0.06	0.01	0.02	0.03	0.01	0.01
450	0.05	0.01	0.01	0.03	0.02	0.01
475	0.03	0.03	0.01	0.01	0.02	0.01
500	0.04	0.01	0.01	0.03	0.03	0.01
SUM	.75	.24	.23	.28	.17	.11

*weight in milligrams

27

Table 7 – Comparison of FT-IR absorption perturbation data (arbitrary units) and filter weights (mg) over three temperature ranges.

	FT-IR absorption perturbation			Filter weight		
	I	II	III	I (partial)	II	III
*JP-5	0.7	0.46	0.66	0.14	0.17	0.18
*Jet A	0.5	0.4	0.35	----	----	----
**JP-5	1.06 ±0.01	0.9 ±0.01	0.86 ±0.09	0.06	0.06	0.06
**JP-5+C_{60}	1.06 ±0.05	0.83 ±0.10	0.89 ±0.07	0.04	0.11	0.1
**Jet A	1.22	0.94	1.02	----	----	----
**Jet A+C_{60}	1.18 ±0.16	0.87 ±0.08	0.93 ±0.07	0.02	0.06	0.04
**Jet A+$C_{60modif.}$	1.59	0.73	0.86	0.02	0.07	0.08

Notes:
* before reactor tube activation
** after reactor tube activation
I(partial): partial sum of 250 to 300 °C
I: sum from 100 to 300 °C
II: sum from 325 to 400 °C
III: sum from 425 to 500 °C

The changeover of the thermal stability between JP-5 and Jet A before and after reactor tube activation is also reflected in the FT-IR absorption spectra (see Figures 15-18). The spectra were calculated using the room temperature single beam spectra as the reference. Before the tube activation, the thermal stressing of JP-5 removes more oxygenated species (OH in the 3100-3600 cm^{-1} and 1650 cm^{-1} as well as ethers in the 1200 cm^{-1} region) relative to Jet A. In fact, an increase can be observed with Jet A in the 1200 cm^{-1} region at elevated temperatures. Conversely, after activation of the reactor tube, significantly more oxygenated functions are removed from Jet A than from JP-5. The compounds removed from both fuels at 500°C (sharp negative bands between 900 and 1000 cm^{-1}) are most probably unsaturated compounds.
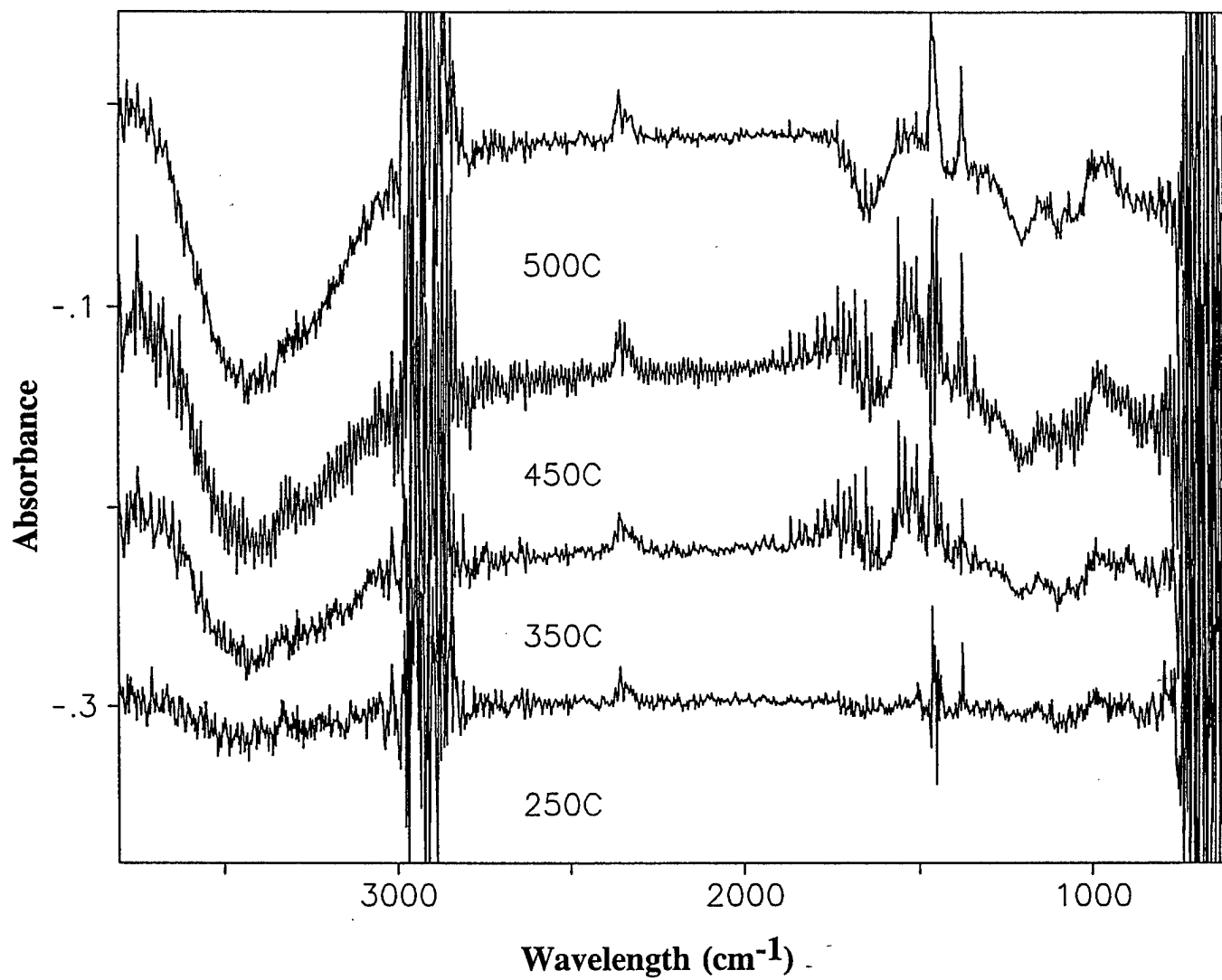
Figure 15. Absorbance (referenced to room temperature) with increasing thermal stressing temperature for JP-5 fuel (before tube activation).
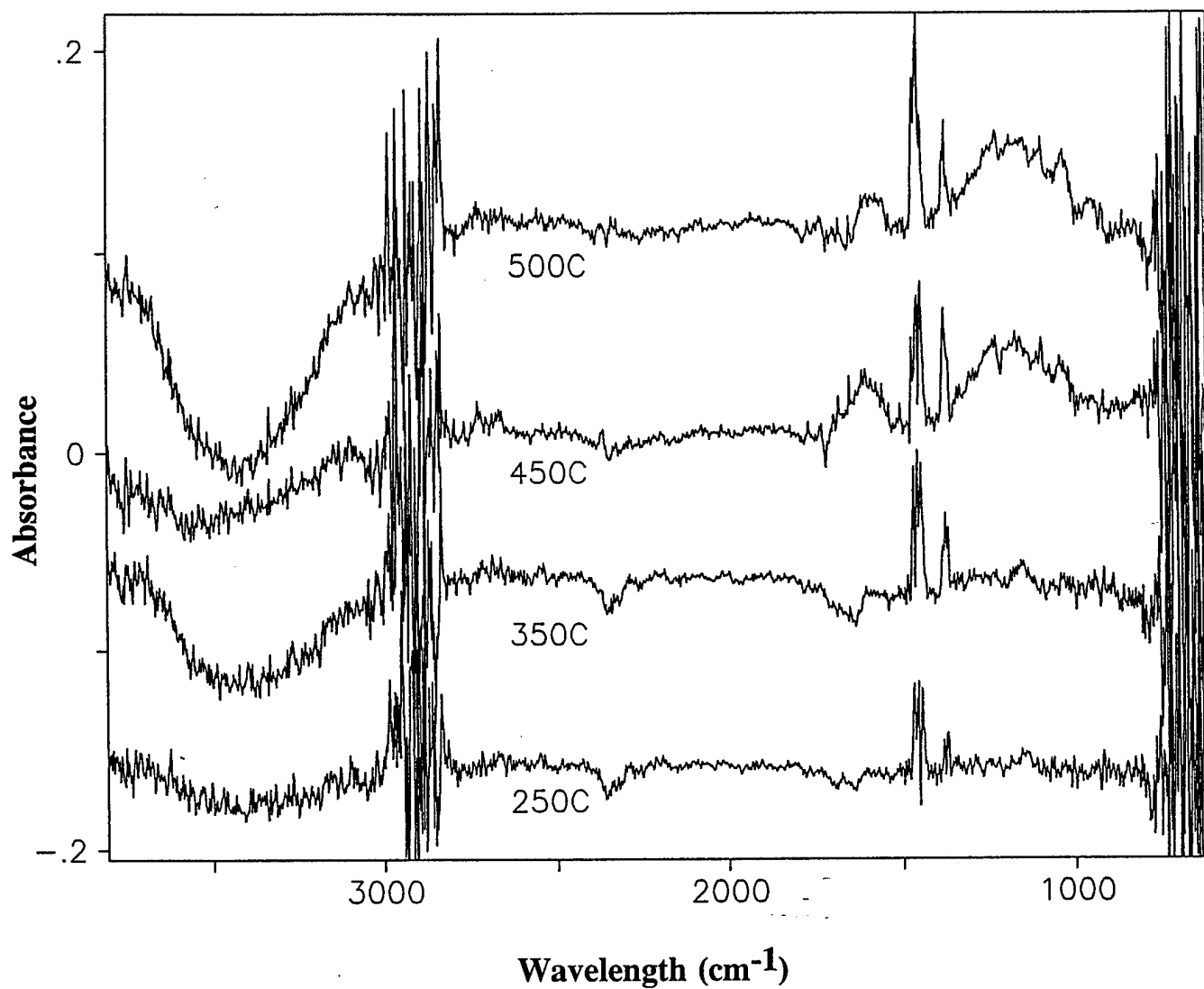
Figure 16. Absorbance (referenced to room temperature) with increasing thermal stressing temperature for Jet A fuel (before tube activation).
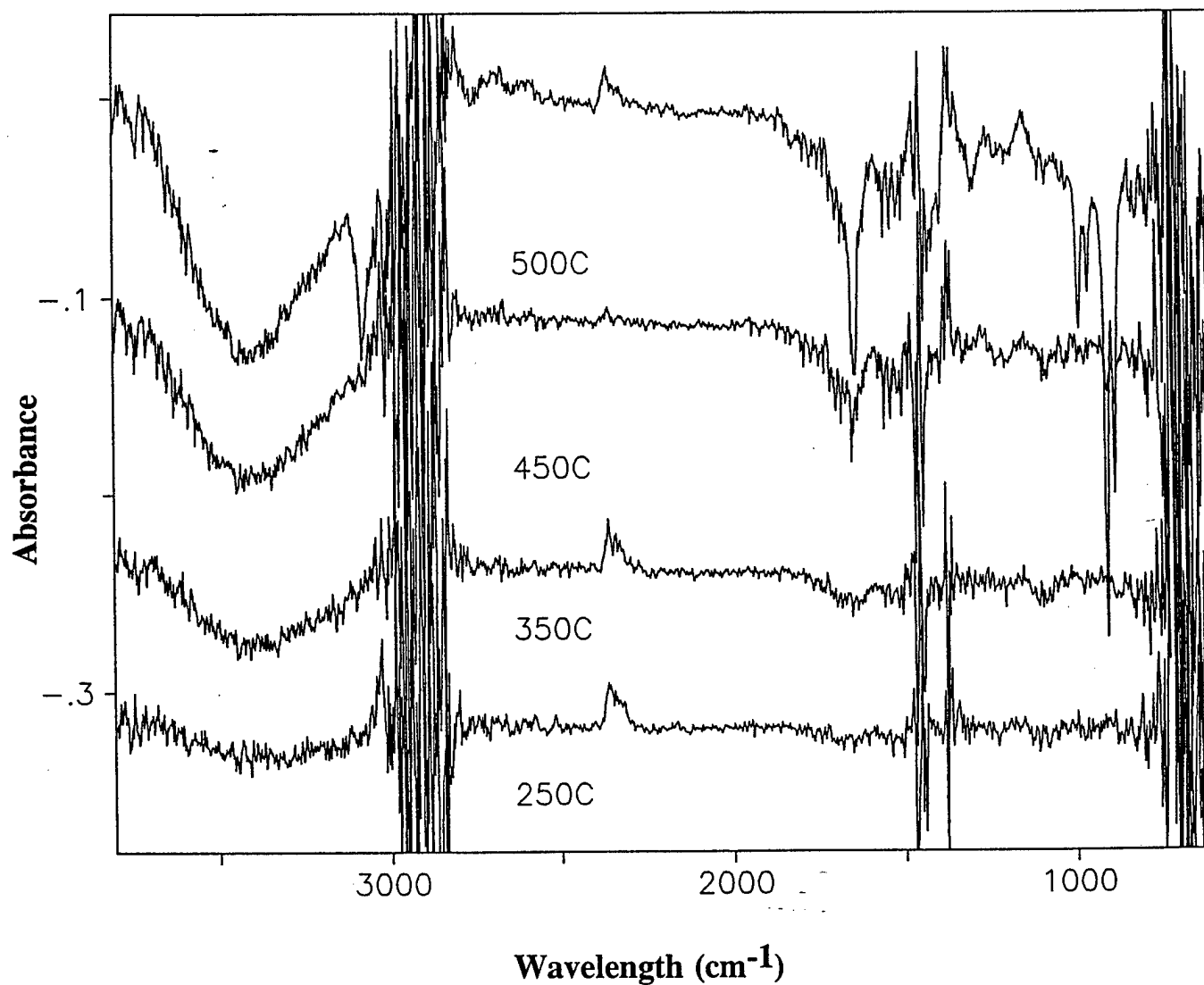
Figure 17. Absorbance (referenced to room temperature) with increasing thermal stressing temperature for JP-5 fuel (after tube activation).
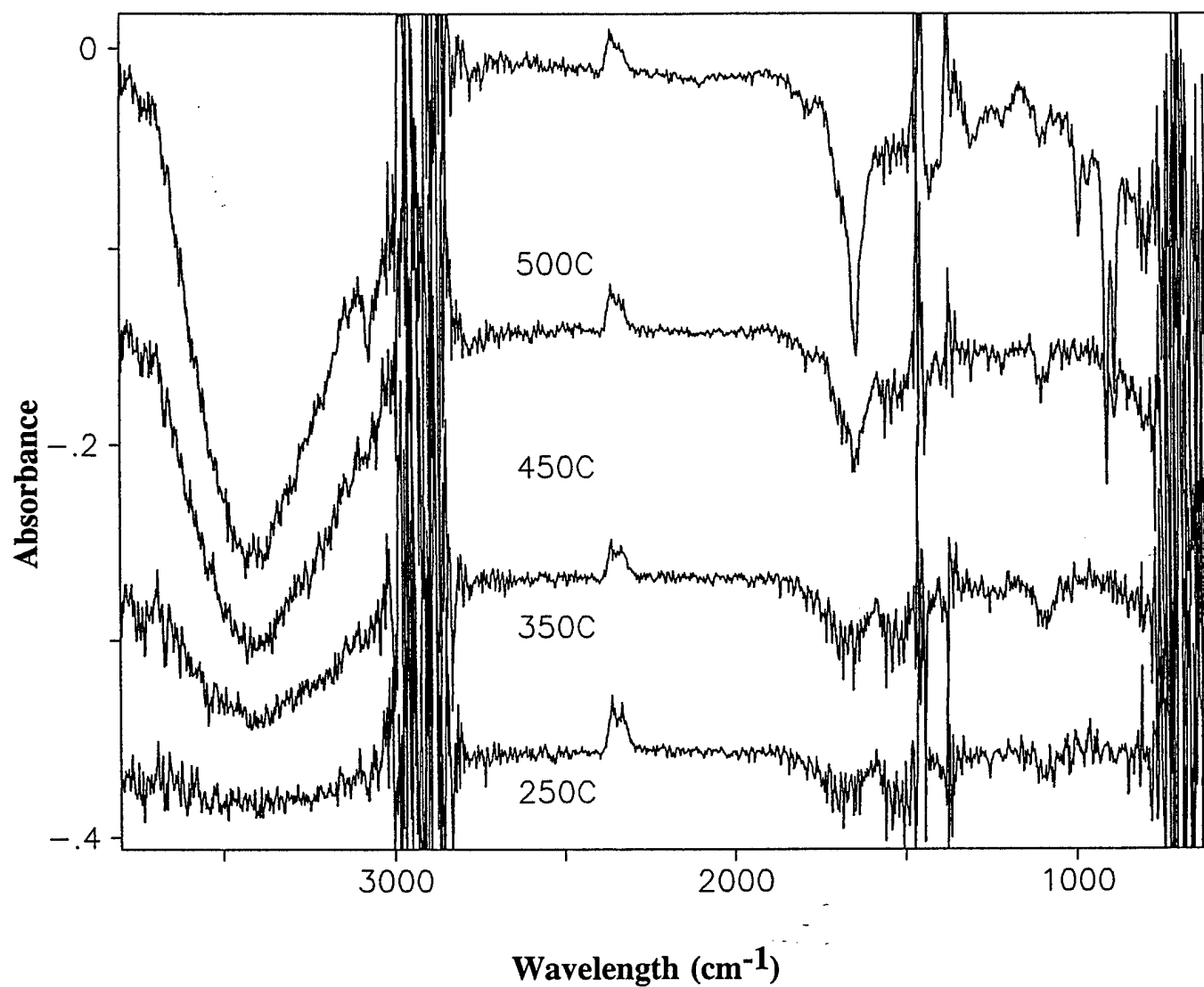
Figure 18. Absorbance (referenced to room temperature) with increasing thermal stressing temperature for Jet A fuel (after tube activation).

The effect of C_{60} doping – An amount of 25 ppm C_{60} or substituted C_{60} (hexylamine) was added to JP-5 and Jet A. The fullerenes were dissolved in toluene (0.4 g/liter). The effect of fullerene doping was studied in the activated tube only. The addition of toluene did not affect the thermal stability of the fuels and the reservoir containing the C_{60} doped jet fuel was kept in the dark to avoid possible photochemical hydroperoxidation.

The data in Table 5 were summed over three different temperature ranges and are shown in Table 7 in order to make it easier to compare the effects of the dopants. According to the FT-IR data in Table 7, the presence of C_{60} slightly improves the thermal stability of JP-5 in the 325-400 °C temperature region, and slightly improves the thermal stability of Jet A in the entire temperature range (room temperature to 500 °C) region. However this improvement is not significant, because it is close to the experimental error.

More dramatic effects can be seen in the FT-IR absorption spectra (Figures 19, 20). Again, in the presence of C_{60} there is less removal of OH in the lower temperature region with Jet A fuel (compare Figure 18 and Figure 20 at 250° C) which nicely correlates with the perturbation data shown in Table 7. It is also interesting, that the sharp negative olefin bands at 910 and 980 cm^{-1}, which occur at 500°C in the activated tube experiments (Figures 17, 18), disappear in the presence of fullerenes for both with JP-5 and Jet A. The characteristic anhydride and C=O bands on Figures 19, 20 are undoubtedly the result of products formed through oxidation reactions catalyzed by C_{60}. The peculiar sharp bands also appearing in the presence of fullerenes at 1180, 1040 and 1020 cm^{-1} could be assigned to aromatic compounds, although with less certainty. If so, then they seem to belong to particular mono and di-substituted benzene derivatives.

## 6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

We have tested the effect of C_{60} and its amine derivatives on the low, medium and high temperature oxidative thermal stability of jet and diesel fuels. The low temperature data from OOP, ICOT, QCM and HPLS tests show that C_{60} generally reduces the deposit formation, although the amount of reduction is only modest (between 5 and 30%). The two amine adducts tested in this study had a deleterious effect, except for JP-5 and diesel fuel in the OOP test. The beneficial effects of C_{60} seem to be larger under more severe conditions, as indicated by temperature or oxidation time (260°C JFTOT or 140°C QCM tests). The severity of the test can also be indicated by oxygen partial pressure. For example, the earlier OOP tests [4] were done in oxygen instead of air and found a more beneficial effect of the C_{60} additive.

In the case of the FT-IR based Fuel Stability Test System (FSTS), where the data were subjected to perturbation analysis for asymmetric wavelet transforms, the best improvements are observed in the medium temperature range (325 to 400 °C), which is consistent with the results for the other tests summarized above. When additional features of the FT-IR absorption spectra are considered (such as the OH region) the benefits are more pronounced in the highest temperature range (425-500 °C), although some potentially deleterious effects also appear to be enhanced at higher temperatures. The effects of the reactor tube activation appeared to be important for this test, as the measured order of stability between the JP-5 and Jet A fuels reversed after tube activation. The amounts of insolubles collected from the FSTS experiments were too small to draw any firm conclusions.

In conclusion, it appears that the stability enhancing effects of pure C_{60} are manifest after the fuel has undergone some initial degradation. It is possible that the C_{60} promotes the formation of compounds which inhibit further oxidation. These effects can be more readily observed under moderate severity conditions. At very high severities, the C_{60} may catalyze or inhibit additional reactions, some of which are beneficial and some of which are deleterious. There appears to be no incentive to use amine derivatives

33
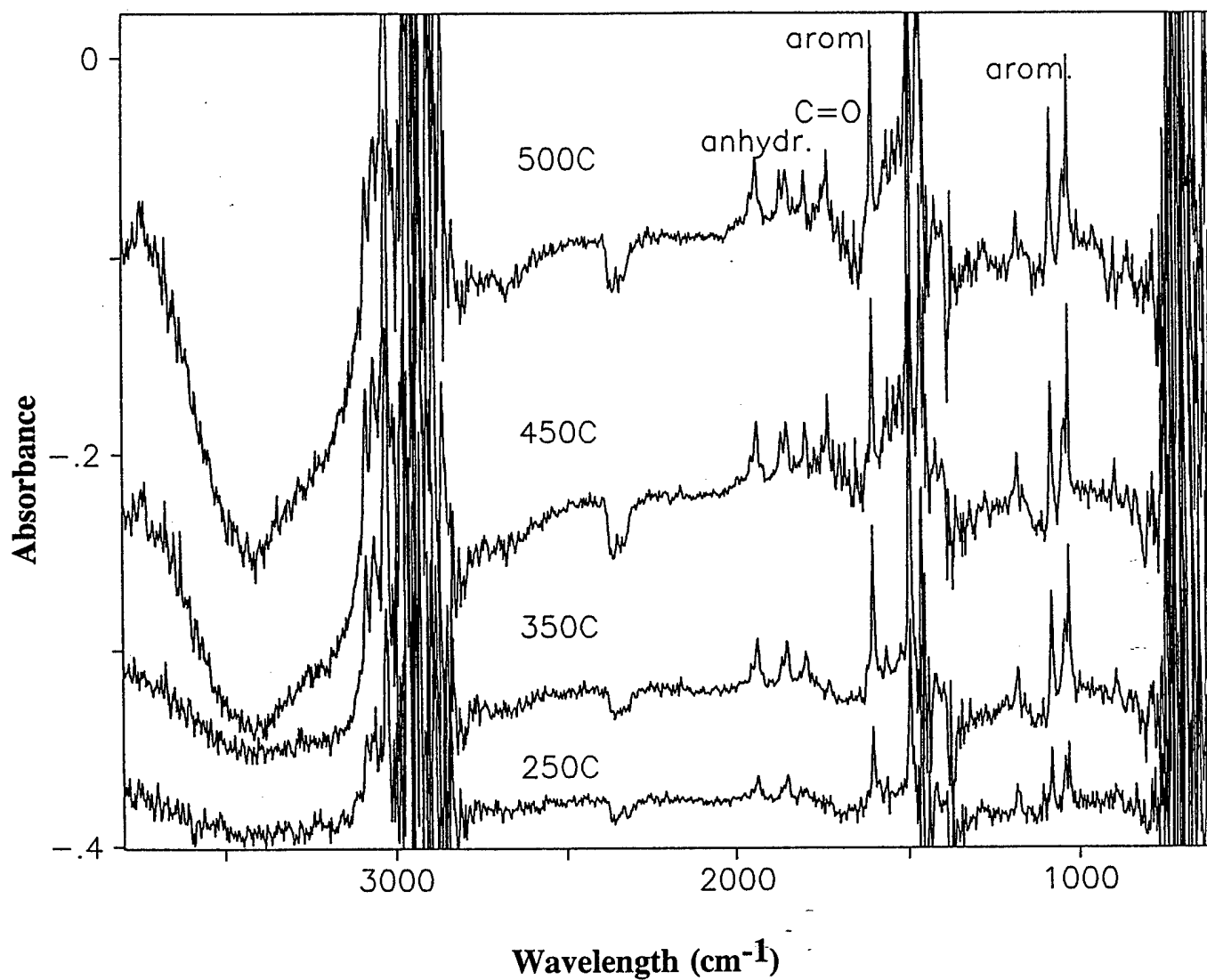
Figure 19. Absorbance (referenced to room temperature) with increasing thermal stressing temperature for JP-5 fuel doped with C_{60} (after tube activation).

34
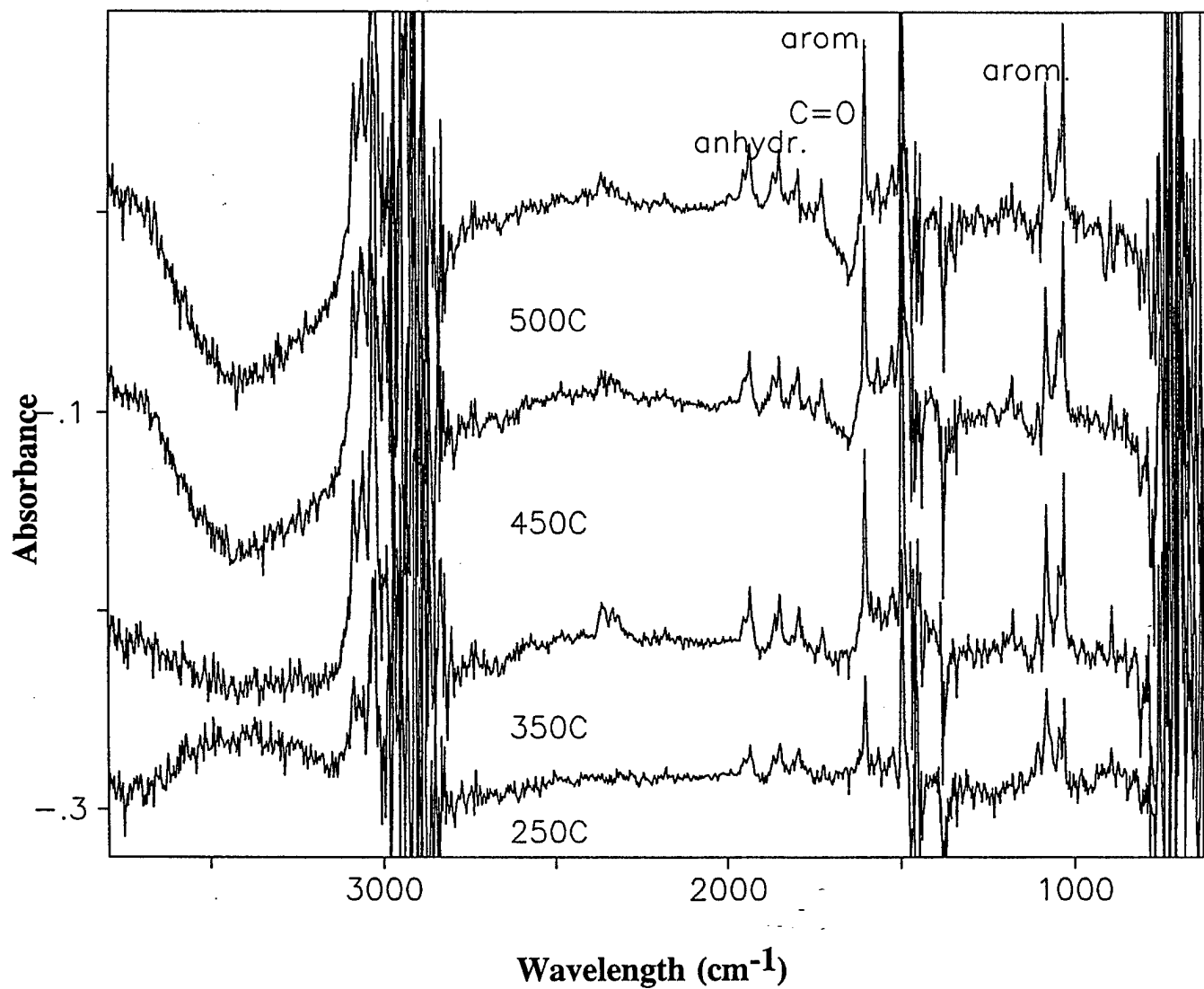
Figure 20. Absorbance (referenced to room temperature) with increasing thermal stressing temperature for Jet A fuel doped with C_{60} (after tube activation).

of C_{60}, except perhaps for certain fuels under a narrow range of conditions. Additional work is warranted on exploring the beneficial temperature ranges for C_{60} which could serve to extend the operating range of common jet fuels. The effects of surface activation in these systems also need further exploration.

6.2. Recommendations for Future Work

For the option task, we propose the following
- Additional OOP tests with pure C_{60} for JP-5 fuel under pure oxygen and at higher temperatures.
- Additional FSTS tests with pure C_{60} and JP-5 at moderate to high temperatures.
- Additional tests to look at effects of tube activation/passivation for the FSTS
- The use of larger quantities of fuel for both types of tests (OOP and FSTS) in order to improve quantitative analysis of fuel degradation products.

7. REFERENCES

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